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Increase of carbon dioxide in the bottom water of the Weddell Sea, Antarctica

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Abstract

High precision total CO_2 (TCO_2) data are presented from the NW Weddell Sea obtained during two cruises which were 3 years apart. A TCO_2 increase from 1993 to 1996 was observed in the newly formed bottom water, whereas no TCO_2 increase was found in the surrounding water masses. Accompanying this TCO_2 increase in the bottom water was an oxygen decrease. Obviously, bottom water with variable characteristics is produced along the margins of the Weddell Sea. Examination of possible causes leads to the conclusion that the bottom water variability is largely due to varying amounts of Warm Deep Water intruding onto the shelves of the Weddell Sea, thus changing the shelf water end-member of bottom water formation. Analysis of the data, using the observed differences of oxygen to perform a correction, suggested that some part of the TCO_2 increase of the bottom water is due to the increased level of anthropogenic CO_2. The TCO_2 increase of the bottom water is commensurate to a tentative annual increase of about 1 μmol kg^{-1} in the surface water source of this bottom water. This would agree fairly well with the increase of the partial pressure of CO_2 in the atmosphere. © 1998 Elsevier Science B.V.

Keywords: Weddell Sea; carbon dioxide; Warm Deep Water; bottom water

1. Introduction

Anthropogenic activity has decisively changed the global carbon cycle, probably leading to adverse effects on the global climate. In the atmosphere the increase of carbon dioxide (CO_2) is dramatic but fortunately also well-documented (Keeling and Whorf, 1994). The magnitude of the CO_2 increase in the atmosphere is ultimately determined by the extent of exchange of CO_2 between the atmospheric reservoir and the other major carbon reservoirs. It is taken for granted that the oceans are pivotal in significantly curtailing the atmospheric CO_2 increase. An increase of the partial pressure of CO_2 in the surface ocean has indeed been established through a major effort covering 10 years of accurate measurements (Inoue et al., 1995). Also, progress is

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made in extracting the anthropogenic CO_2 signal quantitatively from the variable oceanic CO_2 background using indirect methods (Gruber et al., 1996). However, many details of the uptake of CO_2 by the oceans have remained unknown (e.g. Sarmiento, 1993; Francey et al., 1995).

There is still major confusion about the role of the Antarctic Ocean in the global carbon cycle (Tans et al., 1990; Sarmiento et al., 1992). An important reason for this is the lack of data which is largely due to the limited accessibility of the Antarctic Ocean. Large-scale upwelling of CO_2-rich deep water tends to elevate the CO_2 content of the surface layer. On the other hand, CO_2 drawdown is accomplished through the action of photosynthetic activity. Recent investigations seem to point to the dominance of latter mechanism in the Atlantic sector of the Southern Ocean (Hoppema et al., 1995; Bakker et al., 1997), and modeling data suggest similar results for the other sectors (Louanchi et al., 1997). There are strong indications now that ultimately the availability of iron for phytoplankton growth appears to be crucial for the magnitude of the biologically mediated sink (de Baar et al., 1995). Thus, the Antarctic Ocean can be considered to be a sink for atmospheric CO_2 although the exact size of the sink will for the present be a subject of debate. It should be realized that this sink behaviour is due to the competition between physical (upwelling, cooling, advection) and biological (photosynthesis, remineralization) processes. These competing processes would also be active in a non-anthropogenically perturbed Southern Ocean and thus the sink function expresses a natural property of the Southern Ocean. However, the magnitude of the Southern Ocean sink has increased due to the additional uptake of anthropogenic CO_2 from the atmosphere.

Another quality of the Antarctic Ocean is its potential to generate new bottom water, thus ventilating the abyssal world oceans (Mantyla and Reid, 1983). Not only for the global climate this mechanism is of major relevance. The ventilation by dense waters originating from the Antarctic constitutes a conduit for anthropogenic CO_2 to be sequestered in the abyss (Poisson and Chen, 1987; Anderson et al., 1991). It should be noted that the uptake of anthropogenic CO_2 during bottom water formation is a purely physical process. The uptake is achieved in that the shelf water, which is one of the source water masses of the bottom water, equilibrates with the atmosphere to some extent thus also absorbing anthropogenic CO_2. Of the whole Antarctic Ocean the Weddell Sea is the region where the main part of Antarctic Bottom Water originates, i.e. that water mass that fills the deep major ocean basins of the earth. As the newly formed bottom water in the area of investigation in the Weddell Sea is still very young (Gordon et al., 1993; Fahrbach et al., 1995) and thus is promptly replenished, this led us to examine whether differences could be determined in the CO_2 concentration of bottom water sampled during cruises in 1993 and 1996.

2. Sampling and methods

Data are presented from two cruises with the German ice-breaker F.S. Polarstern, one in January 1993 (ANT X/7, Fahrbach, 1994) and one in May 1996 (ANT XIII/4, Fahrbach, 1997). A suite of CO_2, oxygen (O_2) and hydrographic data was obtained on the same transect in the NW Weddell Sea. Water samples were collected with a 24-place General Oceanics rosette sampler that was coupled to a conductivity–temperature–depth instrument. Dissolved oxygen was measured on discrete samples with a standard automated Winkler technique using photometric end-point detection, precision 0.2% CV.

The CO_2 data were obtained by the highly precise coulometric method (Stoll et al., 1993; Dickson and Goyet, 1994), using the same equipment on both cruises. This method measures the total carbon dioxide (TCO_2) concentration, which is the sum of all carbonate species dissolved in seawater, i.e., $TCO_2 = [CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$. Subsamples for the determination of TCO_2 were collected in glass bottles (0.5 l) with flexible screw caps. All analyses were performed within 24 h, but most even within 12 h of sampling. Accuracy on both cruises was set by certified TCO_2 standards (Dickson and Goyet, 1994) made available by Dr. A. Dickson of the Scripps Institution of Oceanography (USA). This ensures full compatibility between both data sets. Before the recent introduction of such reference material large systematical differences between CO_2 data sets were the order of the day (Poisson et al.,

1990). The precision, defined as the difference between all duplicate analyses, amounts to ± 1.0 μmol kg^{-1}. As the accuracy of the standards is about equal (depending on the batch), we conclude that the accuracy of our measurements is somewhat less than the precision.

3. Area description and hydrography

The data originate from a 250 km long transect over the continental slope in the NW Weddell Sea off Joinville Island (Fig. 1), which was occupied both in 1993 and 1996. Along the continental slope of the Antarctic Peninsula, recently formed Weddell Sea Bottom Water (WSBW) is found as a thin bottom layer. WSBW is relatively cold and low-saline as compared to the surrounding water masses (except surface waters). Its origin is further upstream near the shelf break to the south (Gill, 1973; Foster and Carmack, 1976; Fahrbach et al., 1995). It may be produced along the southern and western margins of the Weddell Sea on various locations. The WSBW is

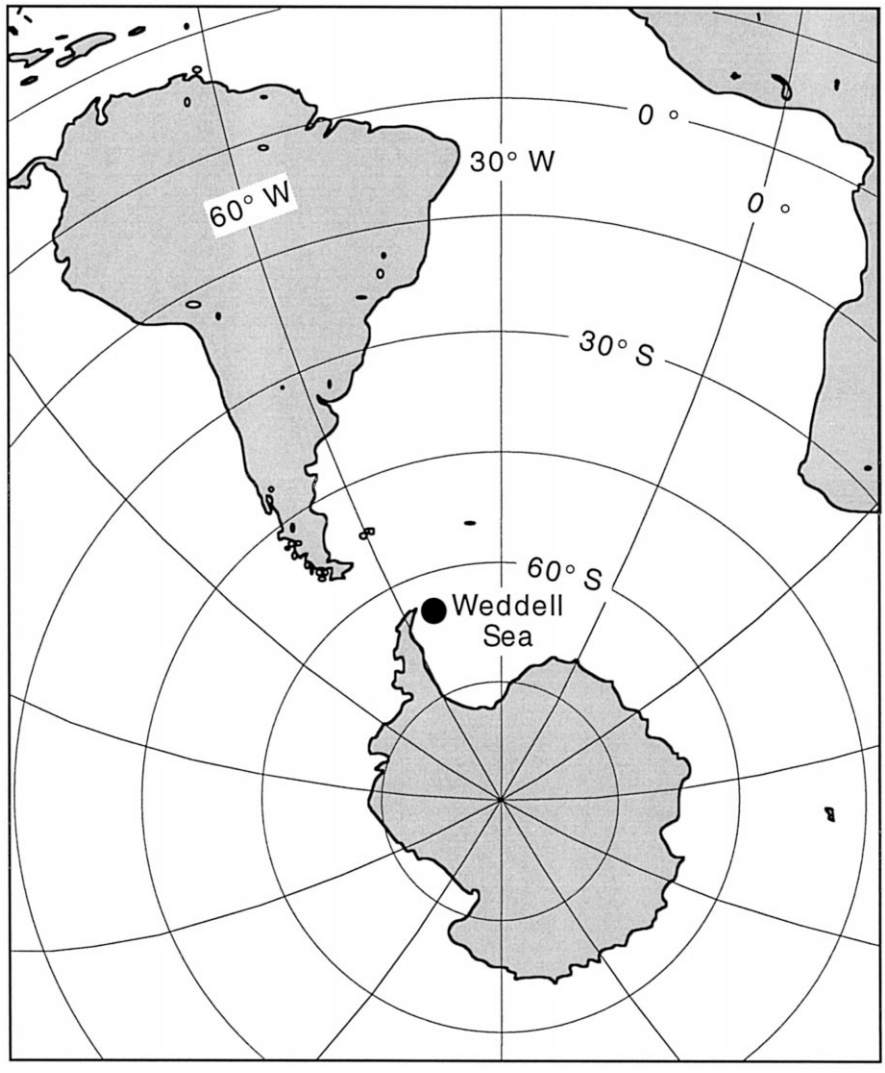

Fig. 1. Map showing the geographical setting around Antarctica with emphasis on the Atlantic sector. The area of investigation off the tip of the Antarctic Peninsula in the the northwestern Weddell Sea is indicated by a large dot.

generated from Western Shelf Water, a high-saline surface water mass, and Warm Deep Water (WDW), which is essentially the only source water mass of the Weddell Sea. A second route of WSBW production is via the Ice Shelf Water (Foldvik et al., 1985), which occurs underneath the vast ice shelves of the southern Weddell Sea. The Ice Shelf Water takes its high density from its extremely low temperature which is below the surface freezing point. On spilling over the shelf break it mixes with WDW to form WSBW.

The newly formed WSBW is hugging the continental slope. During its descent it entrains WDW resulting in a new water mass, the Weddell Sea Deep Water (Fahrbach et al., 1995), which is more saline and less cold than the WSBW. Part of the WSBW leaves the Weddell Sea directly to the north. The remainder descends to the seafloor of the central Weddell Sea and, after mixing, rises to depth levels at which, in a somewhat altered form, it can leave the Weddell Sea (Carmack and Foster, 1975; Locarnini et al., 1993). These processes play a significant role in the ventilation of the world oceans, where the resulting Antarctic Bottom Water can be traced far into the northern hemisphere in all oceans (Broecker and Peng, 1982; Mantyla and Reid, 1983).

4. Results

In Fig. 2 a composite plot of TCO_2 versus the potential temperature (θ) is shown for the years 1993 and 1996 on exactly the same transect in the NW Weddell Sea (see above). This plot results from the mixing between the Warm Deep Water ($\theta > 0.2$–0.3°C) and the near-freezing shelf waters of the

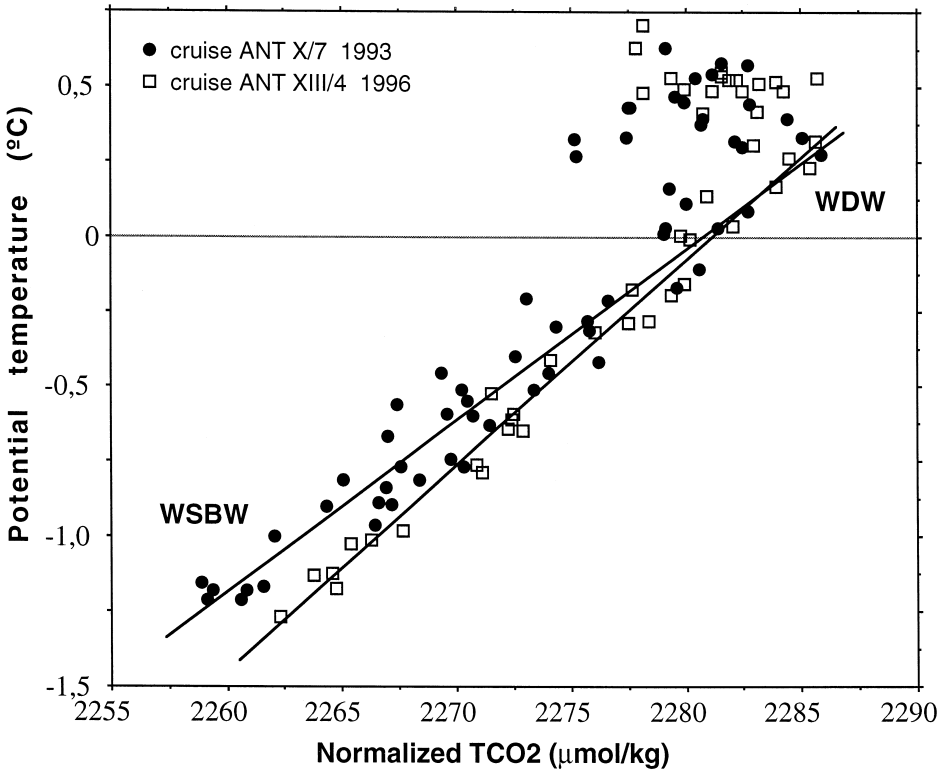

Fig. 2. Plot of total CO_2 against potential temperature for the intermediate and deep water over the continental slope in the NW Weddell Sea. Data from 1993 and 1996. TCO_2 data were normalized to a salinity of 35. For the regression only data points with $\theta < 0.25$°C were used. Regression lines drawn (and the 95% confidence interval for the slopes) are described by $\theta = 0.0570\ (\pm 0.005) * TCO_2 - 130.0409$ ($n = 41$, $r^2 = 0.9314$, $p < 0.0001$) for 1993 and $\theta = 0.0683\ (\pm 0.004) * TCO_2 - 155.8784$ ($n = 28$, $r^2 = 0.9793$, $p < 0.0001$) for 1996. The relationships for the two years are significantly different. WDW is Warm Deep Water, WSBW is Weddell Sea Bottom Water.

Weddell Sea. This mixing sequence produces Weddell Sea Bottom Water ($\theta < -0.7$°C), and the subsequent mixing of WSBW and WDW leads to the most voluminous water body of the Weddell Sea, the Weddell Sea Deep Water (-0.7°C $< \theta < 0.2$°C). The regression lines in this figure were drawn using only the data points with $\theta < 0.25$°C. The reason for this is that at about 0.2–0.3°C the lower boundary of the WDW occurs, which is recognizable by a weak TCO_2 maximum (Hoppema et al., 1997), also discernible in Fig. 2. Hoppema et al. (1997) have shown that the magnitude of this intermediate TCO_2 maximum is approximately constant all along the margins of the Weddell Gyre, i.e. the location where the bottom water formation takes place. All TCO_2 data in Fig. 2 were normalized to a salinity of 35, i.e. normalized $TCO_2 = TCO_2 * (35/S)$. The motivation for this is that the relative TCO_2 changes in the Weddell Sea are of similar magnitude as the salinity changes. As corresponding water masses in both years of which data are shown in Fig. 2 may have slightly different salinities, this would also result in different TCO_2 values. As we are not interested in such differences they were catered for through normalization. It should be added that the effect of salinity variations on the data shown in Fig. 2 is minor since essentially the same composite plot is obtained without normalizing the TCO_2 data.

Note in Fig. 2 that within the WDW at higher θ the scatter of the TCO_2 values is large. This is due to the mixing of the upper segment of the WDW (having higher temperatures) with the onshore surface waters around the shelf break (Hoppema et al., 1997). It should be stressed that this higher segment of the WDW does not necessarily participate in the bottom water formation process. In fact, the mixing

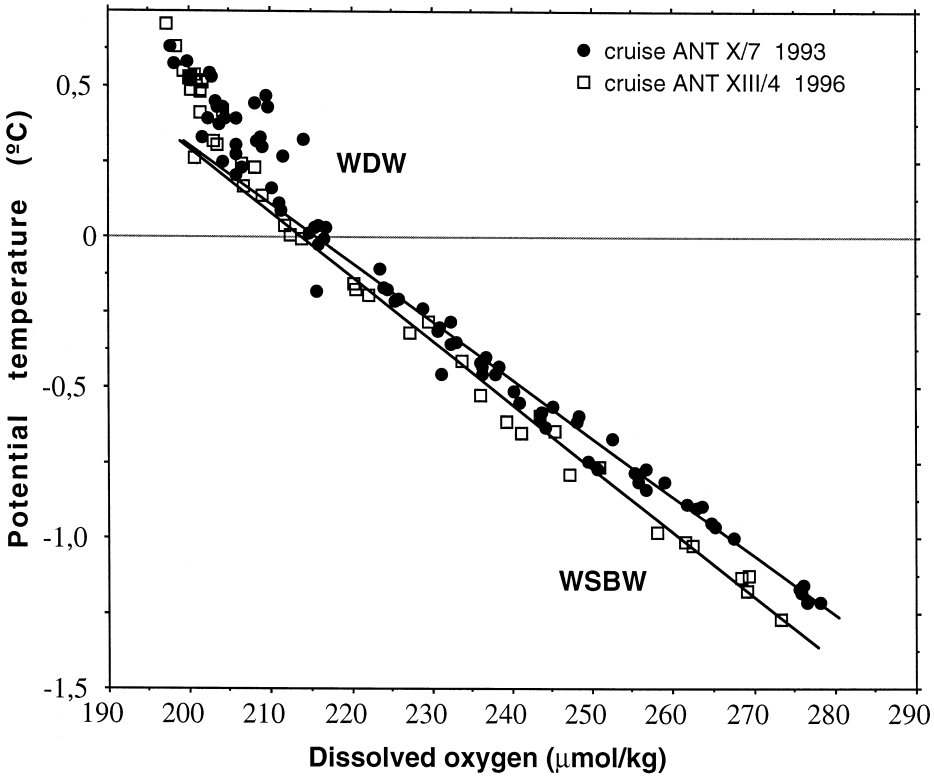

Fig. 3. Plot of dissolved oxygen against potential temperature for the intermediate and deep water over the continental slope in the NW Weddell Sea. Oxygen data were not normalized because the influence of salinity variations on oxygen is negligible. Regression lines drawn (and the 95% confidence interval for the slopes) are described by $\theta = -0.0194\ (\pm 0.0006) * O_2 + 4.1801$ ($n = 58$, $r^2 = 0.9865$, $p < 0.0001$) for 1993 and $\theta = -0.0213\ (\pm 0.0008) * O_2 + 4.5525$ ($n = 27$, $r^2 = 0.9920$, $p < 0.0001$) for 1996. Both relationships are significantly different. WDW is Warm Deep Water, WSBW is Weddell Sea Bottom Water.

plot (Fig. 2) suggests that mixing can be considered to occur between the lower WDW close to the TCO_2 maximum and some surface water end-member. Also note that the scatter of the TCO_2 data around the regression lines in Fig. 2, particularly for the 1993 data, is larger than the analytical precision of the measurements. This scatter is due to the fact that there are multiple sources of WSBW along the southern and western margins of the Weddell Sea (Gordon et al., 1993; Fahrbach et al., 1995). Each of these sources of bottom water may have slightly different concentrations of TCO_2 (and other constituents) and different temperature and salinity. Variability of the ratios of these different sources of WSBW will effectuate the occurrence of scatter. It should be noted that although these various sources of WSBW do cause the data to be scattered to some extent, Fig. 2 evidences that our approximation appears to be valid, i.e. the data can be considered to result from the mixing between the two end-members WDW and shelf water.

While both for 1993 and 1996 highly significant linear relationships between TCO_2 and θ are constructed, they possess significantly different slopes (Fig. 2). In the high-temperature range of the linear region of the plot the data points of both years largely overlap, whereas in the WSBW range the difference becomes unequivocal: the TCO_2 concentration in the bottom water is higher in 1996 than in 1993. This increase of the TCO_2 concentration in the WSBW between 1993 and 1996 may well reflect an increased amount of anthropogenic CO_2 in the surface water end-member of 1996 compared to 1993. However, another cause could be different compositions of the source water masses in generating WSBW. Latter remark particularly points to the possibility that in 1996 the surface water involved in the bottom water formation process could have a higher TCO_2 than that in 1993 due to causes of non-anthropogenic nature. We assess variation of the WDW source concentration to be unimportant because Fig. 2 reveals that the TCO_2 concentration of the WDW end-member appears to be constant.

A means to decide whether variability of the source water masses of the WSBW does play a part is the plotting of other constituents whose possible variations are with certainty not the consequence of anthropogenic causes. Candidate constituents are the nutrients and dissolved oxygen (O_2). The corresponding composite $O_2-\theta$ diagram is displayed in Fig. 3. If the composition of the WSBW in 1993 and 1996 were equal, identical $O_2-\theta$ relationships for both years would be expected since the O_2 concentration in the surface water does not have an anthropogenic component. However, it is apparent that, similar to TCO_2, the $O_2-\theta$ relationships are significantly different, with the bottom water containing less O_2 in 1996 than in 1993 (Fig. 3). These observations thus indicate that the formation process along the shelf break and continental slope results in WSBW of variable characteristics, which may be expressed as interannual variation. Distinct interannual variability in bottom water properties has previously been reported for the northern Weddell Sea by Foster and Middleton (1979).

5. Discussion

The variation of WSBW characteristics carries back to the variation of its shelf water source (Figs. 2 and 3). There are several processes that may effectuate the variation of TCO_2 and O_2 in the shelf water that participates in the bottom water production:

(1) Differences in the extent of equilibration of the surface water with the atmosphere: Dense shelf water is produced through cooling, followed by sea ice formation through which the salt content of the underlying water is enhanced. During this (autumn) cooling the solubility of CO_2 and O_2 increases, resulting in lower partial pressure of CO_2 and lower O_2 saturation which in turn leads to the uptake of these gases from the atmosphere. In fact, undersaturation for both CO_2 and O_2 has been reported for the shelf waters that are involved in the bottom water formation process (Anderson et al., 1991). Were this process dominant in causing variability in the TCO_2 and O_2 concentrations of the shelf water, deviations of O_2 and TCO_2 between the different years would be in the same sense, which, however, is not the case in Figs. 2 and 3.

(2) Biological activity: A small O_2 depletion has been reported for the WSBW of the Weddell Sea (Rutgers van der Loeff and van Bennekom, 1989) which would point to biological activity in the WSBW. However, latter authors show that this O_2

depletion correlates well with a silicate enrichment in the WSBW, while at the same time they convincingly demonstrate that no silicate enrichment occurs during the process of bottom water formation. This allows us to conclude that no O_2 depletion occurs during the formation of bottom water. Rather, the O_2 depletion develops, like the silicate enrichment, in the bottom layer of the central Weddell Sea (Rutgers van der Loeff and van Bennekom, 1989). Data in the present study are neither indicative of biological activity in the WSBW: calculating the concentration ratio $\Delta(O_2(1996) - O_2(1993))/\Delta(TCO_2(1996) - TCO_2(1993))$ at 1.1°C (Figs. 2 and 3; or for the extrapolated shelf water end-member, see Table 1 below), a value of -1.66 is found for the relative O_2 to TCO_2 changes between 1993 and 1996. If biological processes were prevalent a ratio of about -1.45 (Anderson and Sarmiento, 1994) or, more traditionally, -1.30 (Redfield et al., 1963) would be expected. Thus, biological activity does probably not significantly affect the composition of the bottom water during its formation process and hence, cannot explain the observed differences in Figs. 2 and 3.

(3) Exchange of constituents across the sediment–water interface: On the seafloor decay products of organic matter could accumulate which may be delivered to the overlying water column, and then possibly during the process of bottom water formation. In the literature conflicting views are found. Jacobs (1989) and Rutgers van der Loeff and van Bennekom (1989) conclude that the shelf sediments do not significantly contribute to the concentration of constituents in the shelf water, whereas Gammelsrød et al. (1994) contend the opposite. Based on shelf data collected by us during austral winter in the Weddell Sea (Hoppema et al., 1995), we must conclude that the contentions of Gammelsrød et al. (1994), which were deduced from property–salinity plots of summer shelf data, cannot be corroborated. Thus, we attach more value to the aforementioned conclusions of Jacobs (1989) and Rutgers van der Loeff and van Bennekom (1989) and infer that exchange of constituents across the sediment–water interface on the shelves is negligible.

(4) A fourth mechanism creating variable shelf water characteristics is the irregular occurrence of intrusions of WDW onto the shelves. All along the margins of the Weddell Sea WDW intrudes onto the shelves without directly contributing to the process of bottom water formation (Gill, 1973; Foster and Carmack, 1976; Jacobs, 1991). This is one of the important mechanisms determining the characteristics of the shelf waters (Fahrbach et al., 1994). Intrusion of WDW onto the shelves is dependent on an intricate interplay of factors such as the local topography and meteorology, which readily leads to variations in the amount of WDW admixing on the shelves, in turn causing variations in the properties of the shelf waters. It is worth adding that also varying property values of the intruding WDW could cause such an effect. For instance, in 1993 and 1996 the WDW cores had somewhat different salinity and temperature characteristics (Fahrbach, 1997). As WDW is rich in TCO_2 and poor in O_2, variable amounts of WDW in the shelf water would indeed cause opposite changes of these properties as seen in Figs. 2 and 3.

Of the four aforementioned possibilities of WSBW variability the latter is obviously most apt for explaining our observations. Foster and Middleton (1979) also make plausible that the WSBW variability they observed was caused through varying ratios of WDW and shelf water in the preconditioning stages of the bottom water production.

Due to the variability of the bottom water it is impossible to decide in an uncomplicated way whether the increase of the TCO_2 concentration in the WSBW between 1993 and 1996 (Fig. 2) was solely generated by natural variability, or the in-

Table 1
End-members of mixing for 1993 and 1996

	O_2(1993) (μmol kg^{-1})	O_2(1996) (μmol kg^{-1})	TCO_2(1993) (μmol kg^{-1})	TCO_2(1996) (μmol kg^{-1})
Shelf water	310.8	300.6	2249.0	2255.2
WDW	202.6	202.0	2285.8	2285.9

The end-members were obtained through extrapolation of the relationships depicted in Figs. 2 and 3, for the WDW to a potential temperature of 0.25°C and for the shelf water to -1.85°C. TCO_2 values were normalized to a salinity of 35. WDW is Warm Deep Water.

creased burden of anthropogenic CO_2 in the shelf water played a part as well. However, compared to the huge natural variations of CO_2 in the surface oceans that usually thwart its proper investigation, we may only be faced with a minor complication. We can in fact overcome the variable composition of the bottom water. As argued above, the different WSBW characteristics for both years stem from different amounts of WDW that are incorporated into the shelf water end-member *prior to* the actual formation of bottom water. The oceanographic processes behind this analysis should be clarified as the participation of only two end-members (shelf water and WDW) might lead to the impression that it is impossible to form different mixing lines as seen in Figs. 2 and 3: when WDW intrudes onto the shelf a mixing product is formed with intermediate TCO_2, O_2 and temperature characteristics on the mixing line between WDW and shelf water. On the shelf this mixing product (which is the new, modified shelf water) is cooled down to the freezing point before it will be involved in the bottom water formation process. Through this cooling, which of course is a non-conservative process, the new shelf water is not lying on the original mixing line anymore. If in two different years the amount of WDW intruded onto the shelves has been different, the resulting shelf waters will have different signatures. Upon mixing during the actual process of bottom water formation (which only occurs on some specific locations) these different shelf waters produce specific mixing lines. The purpose of our analysis is to determine the dissimilar fraction of WDW that has intruded onto the shelves for the years 1993 and 1996. This WDW fraction, that can be used to correct the TCO_2–θ relationships, is quantifiable in the following way.

In our analysis the WSBW formation is treated as a mixing process between two end-members, WDW and near-freezing point shelf water. Given the highly significant linear relationships in Figs. 2 and 3, this approach appears to be valid. As the bottom water has the higher TCO_2 and lower O_2 in 1996 compared to 1993 this implies that the ratio of WDW to surface water in the shelf water end-member had been larger in 1996 than in 1993. Starting from the mixing diagram of 1993, the elevated contribution of WDW to the mixing sequence in 1996 is calculated using the O_2–θ relationships (Fig. 3). The end-members of mixing that go into the calculation appear in Table 1. There is excellent agreement between the values of the WDW end-member for both years. This is a fine manifestation of the constancy of the WDW end-member. The additional fraction of WDW in 1996 (A) as compared to 1993 is extracted from the following equation:

$$A * [\mathrm{WDW}] + (1 - A) * [\mathrm{SW}(1993)] = [\mathrm{SW}(1996)] \quad (1)$$

where [WDW] is the WDW concentration, [SW(1993)] the shelf water of 1993, and [SW(1996)] the shelf water of 1996. Substituting the appropriate O_2 concentrations (Table 1) into this equation yields $A = 0.094$. Thus, the shelf water end-member of 1996 can be regarded as being made up of 90.6% of shelf water of 1993 plus 9.4% of WDW. Recapitulating, this signifies that in 1996 more WDW has intruded onto the shelves *prior to* the actual process of bottom water formation, thus increasing the TCO_2 and decreasing the O_2 concentrations of the shelf water end-member. Solving Eq. (1) for TCO_2 (concentrations in Table 1) and using these fractions, the TCO_2 value of the shelf water end-member in 1996, [SW(1996)], is calculated to be 2252.5 μmol kg^{-1}. We can think of latter value as being the shelf water end-member of 1996 which has been corrected for an elevated contribution of WDW and thus as if adapted to the 1993 base line.

With this corrected value of 2252.5 μmol kg^{-1}, the TCO_2 shelf water end-member of 1996 is higher than that of 1993 (Table 1) by 3.5 μmol kg^{-1} (instead of 6.2 μmol kg^{-1} before the correction; Table 1). As this value is obtained by an extrapolation procedure which could give rise to large errors, the significance of this figure should be taken in contemplation. We assess the actual error to be much smaller than a possible formal error due to the extrapolation. This is based on earlier observations in the Weddell Sea in mid-winter which exhibit TCO_2 and O_2 concentrations in the surface layer that are very similar to those data obtained in the present study (Hoppema et al., 1995; and additional data). Although it is hard to assess the significance of the calculated TCO_2 increase in the shelf water to the full extent, we are confident that the increase as such is real. Additional support for this assessment appears below.

We conclude that the WSBW changes between 1993 and 1996 are at least partly caused by an increase of the TCO_2 in the shelf water end-member of the WSBW. Several other possible causes having been excluded (see above), the enhanced uptake of anthropogenic CO_2 from the atmosphere by the shelf waters is invoked to be the ultimate cause of the WSBW changes. With the calculated TCO_2 increase of 3.5 μmol kg^{-1} the annual TCO_2 increase of the shelf water is 1.1–1.2 μmol kg^{-1}. Latter figure is in fair agreement with the annual increase of atmospheric CO_2 of 1.4 ppm at the south pole during the late 1980s and early 1990s (Keeling and Whorf, 1994; Thoning et al., 1994), which would theoretically give rise to a TCO_2 increase of 0.9 μmol kg^{-1} (Dyrssen and Wedborg, 1982).

Our data reveal that an anthropogenic CO_2 signal in the WSBW could be determined within a time span as short as three years. The western Weddell Sea appears to be the ideal site for such an investigation because the bottom water has a short residence time and is only to a minor extent diluted with other water masses devoid of anthropogenic CO_2. In addition, possible non-anthropogenic causes of bottom water variability, which in other ocean regions induce large sources of uncertainty, have effectively been removed through natural mechanisms (see above). It would be advisable to exploit a time-record of the invasion of anthropogenic CO_2 right in this area. Future research could focus on the reconciliation of this time-record with different other methods calculating the anthropogenic CO_2 signal (Poisson and Chen, 1987; Anderson et al., 1991; Gruber et al., 1996). This would also enable us to track the anthropogenic signal in the Weddell Sea and the abyssal oceans. In addition, a time-record of anthropogenic CO_2 could serve as a verification of ocean circulation models in calculating the anthropogenic CO_2 signal. Its importance will far surpass the local nature of the measurements due to the Weddell Sea's pivotal role in the ventilation of the world oceans.

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References

Anderson, L.A., Sarmiento, J.L., 1994. Redfield ratios of remineralization determined by nutrient data analysis. Global Biogeochem. Cycles 8, 65–80.

Anderson, L.G., Holby, O., Lindegren, R., Ohlson, M., 1991. The transport of anthropogenic carbon dioxide into the Weddell Sea. J. Geophys. Res. C 96, 16679–16687.

de Baar, H.J.W., de Jong, J.T.M., Bakker, D.C.E., Löscher, B.M., Veth, C., Bathmann, U., Smetacek, V., 1995. Importance of iron for phytoplankton spring blooms and CO_2 drawdown in the Southern Ocean. Nature 373, 412–415.

Bakker, D.C.E., de Baar, H.J.W., Bathmann, U.V., 1997. Changes of carbon dioxide in surface waters during spring in the Southern Ocean. Deep-Sea Res. II 44, 91–127.

Broecker, W.S., Peng, T.-H., 1982. Tracers in the Sea. Eldigio Press, Palisades, NY, 690 pp.

Carmack, E.C., Foster, T.D., 1975. On the flow of water out of the Weddell Sea. Deep-Sea Res. 22, 711–724.

Dickson, A.G., Goyet, C. (Eds.), DOE, 1994. Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water; Version 2, ORNL/CDIAC-74.

Dyrssen, D., Wedborg, M., 1982. The influence of the partial pressure of carbon dioxide on the total carbonate of seawater. Mar. Chem. 11, 183–185.

Fahrbach, E. (Ed.), 1994. Cruise Report ANT X/7. Berichte zur Polarforschung, vol. 135, pp. 127–197.

Fahrbach, E. (Ed.), 1997. Cruise report ANT XIII/4. Berichte zur Polarforschung. In preparation.

Fahrbach, E., Peterson, R.G., Rohardt, G., Schlosser, P., Bayer, R., 1994. Suppression of bottom water formation in the southeastern Weddell Sea. Deep-Sea Res. I 41, 389–411.

Fahrbach, E., Rohardt, G., Scheele, N., Schröder, M., Strass, V., Wisotzki, A., 1995. Formation and discharge of deep and bottom water in the northwestern Weddell Sea. J. Mar. Res. 53, 515–538.

Foldvik, A., Gammelsrød, T., Tørresen, T., 1985. Physical oceanography studies in the Weddell Sea during the Norwegian Antarctic Research Expedition 1978/79. Polar Res. 3 n.s., 195–207.

Foster, T.D., Carmack, E.C., 1976. Frontal zone mixing and Antarctic bottom water formation in the southern Weddell Sea. Deep-Sea Res. 23, 301–317.

Foster, T.D., Middleton, J.H., 1979. Variability in the bottom water of the Weddell Sea. Deep-Sea Res. A 26, 743–762.

Francey, R.J., Tans, P.P., Allison, C.E., Enting, I.G., White, J.W.C., Trolier, M., 1995. Changes in oceanic and terrestrial carbon uptake since 1982. Nature 373, 326–330.

Gammelsrød, T., Foldvik, A., Nøst, O.A., Skagseth, O, Anderson, L.G., Fogelqvist, E., Olsson, K., Tanhua, T., Jones, E.P., Osterhus, S., 1994. Distribution of water masses on the conti-

nental shelf in the southern Weddell Sea. In: Johannessen, O.M., Muench, R.D., Overland, J.E. (Eds.), The polar oceans and their role in shaping the global environment, Geophysical Monograph 85, American Geophysical Union, Washington, DC, pp. 159–176.

Gill, A.E., 1973. Circulation and bottom water production in the Weddell Sea. Deep-Sea Res. 20, 111–140.

Gordon, A.L., Huber, B.A., Hellmer, H.H., Ffield, A., 1993. Deep and bottom water of the Weddell Sea's western rim. Science 262, 95–97.

Gruber, N., Sarmiento, J.L., Stocker, T.F., 1996. An improved method for detecting anthropogenic CO_2 in the oceans. Global Biogeochem. Cycles 10, 809–837.

Hoppema, M., Fahrbach, E., Schröder, M., Wisotzki, A., de Baar, H.J.W., 1995. Winter–summer differences of carbon dioxide and oxygen in the Weddell Sea surface layer. Mar. Chem. 51, 177–192.

Hoppema, M., Fahrbach, E., Schröder, M., 1997. On the total carbondioxide and oxygen signature of the circumpolar deep water in the Weddell Gyre. Oceanol. Acta 20. In press.

Inoue, H.Y., Matsueda, H., Ishii, M., Fushimi, K., Hirota, M., Asanuma, I., Takasugi, Y., 1995. Long-term trend of the partial pressure of carbon dioxide (pCO_2) in surface waters of the western North Pacific, 1984–1993. Tellus B 47, 391–413.

Jacobs, S.S., 1989. Marine controls on modern sedimentation on the Antarctic continental shelf. Mar. Geol. 85, 121–153.

Jacobs, S.S., 1991. On the nature and significance of the Antarctic slope front. Mar. Chem. 35, 9–24.

Keeling, C.D., Whorf, T.P., 1994. Atmospheric CO_2 records from sites in the SIO air sampling network. In: Boden, T.A., Kaiser, D.P., Sepanski, R.J., Stoss, F.W. (Eds.), Trends'93: A compendium of data on global change. Carbon dioxide Information Analysis Center, ORNL, Oak Ridge, Tenn., pp. 16–26.

Locarnini, R.A., Whitworth, T. III, Nowlin Jr, W.D., 1993. The importance of the Scotia Sea on the outflow of Weddell Sea deep water. J. Mar. Res. 51, 135–153.

Louanchi, F., Hoppema, M., Wolf-Gladrow, D., Ruiz-Pino, D., 1997. The southern ocean is a substantial sink for atmospheric CO_2. Global Biogeochem. Cycles. Submitted.

Mantyla, A.W., Reid, J.L., 1983. Abyssal characteristics of the World Ocean waters. Deep-Sea Res. A 30, 805–833.

Poisson, A., Chen, C.-T.A., 1987. Why is there little anthropogenic CO_2 in the Antarctic bottom water?. Deep-Sea Res. 34, 1255–1275.

Poisson, A., Culkin, F., Rideout, P., 1990. Intercomparison of CO_2 measurements. Deep-Sea Res. 37, 1647–1650.

Redfield, A.C., Ketchum, B.H., Richards, F.A., 1963. The influence of organisms on the composition of seawater. In: Hill, M.N. (Ed.), The Sea, vol. 2. Interscience, New York, pp. 26–77.

Rutgers van der Loeff, M.M., van Bennekom, A.J., 1989. Weddell Sea contributes little to silicate enrichment in Antarctic bottom water. Deep-Sea Res. 36, 1341–1357.

Sarmiento, J.L., 1993. Atmospheric CO_2 stalled. Nature 365, 697–698.

Sarmiento, J.L., Orr, J.C., Siegenthaler, U., 1992. A perturbation simulation of CO_2 uptake in an ocean general circulation model. J. Geophys. Res. C 97, 3621–3645.

Stoll, M.H.C., Rommets, J.W., de Baar, H.J.W., 1993. Effect of selected calculation routines and dissociation constants on the determination of total carbon dioxide in seawater. Deep-Sea Res. 40, 1307–1322.

Tans, P.P., Fung, I.Y., Takahashi, T., 1990. Observational constraints on the global atmospheric CO_2 budget. Science 247, 1431–1438.

Thoning, K.W., Tans, P.P., Waterman, L.S., 1994. Atmospheric CO_2 records from sites in the NOAA/CMDL continuous monitoring network. In: Boden, T.A., Kaiser, D.P., Sepanski, R.J., Stoss, F.W. (Eds.), Trends'93: A compendium of data on global change, Carbon Dioxide Information Analysis Center, ORNL, Oak Ridge, Tenn., pp. 28–40.